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# RPPR Final Report
as of 09-Nov-2018

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**STEM Participants:**

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**Participant Type:** PD/PI
**Participant:** Krista Walton
**Person Months Worked:** 1.00

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International Collaboration:
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**Participant Type:** Graduate Student (research assistant)
**Participant:** William Mounfield III
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**Participant Type:** Graduate Student (research assistant)
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**Authors:** William P. Mounfield, Micaela Taborga Claure, Pradeep K. Agrawal, Christopher W. Jones, Krista S. Wa
**Keywords:** ammonia adsorption
**Abstract:** A hydrotalcite-derived MgAl oxide (MMO) was evaluated in combination with the metal?organic frameworks (MOFs) UiO-66 and UiO-66- NH2 for the adsorption of ammonia. Analysis of the materials' textural properties after ammonia breakthrough adsorption revealed no change in the PXRD patterns or FTIR spectra; however, a slight decrease in surface area was observed, consistent with the hypothesized presence of strongly adsorbed species after adsorption. UiO-66:MMO and UiO-66-NH2:MMO composites maintained ammonia adsorption capacity under dry conditions. An almost 2-fold increase in humid ammonia capacity was observed for the UiO-66:MMO composite, far beyond that expected through a linear combination of the two materials' capacities. The synergistic effect observed in humid conditions was further investigated with water adsorption experiments, which suggested the effect is the result of the high water affinity of MMO.
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**Authors:** William Mounfield
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**RPPR Final Report**
as of 09-Nov-2018

# ADVANCED PROCESSING OF MULTIFUNCTIONAL MATERIALS FOR ADSORPTIVE REMOVAL AND SENSING OF CHEMICAL WARFARE AGENTS

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## 1.0 OVERVIEW, BACKGROUND, AND OBJECTIVES

### 1.1 OVERVIEW

The ability to manipulate and control matter at the nanoscale offers the potential for radical advances in how we produce chemicals, materials, and energy. The design of nanoscale structures provides access to physicochemical properties that are distinctly different and unattainable compared to the bulk phase. This control at the nanoscale is critical for advancing a broad spectrum of technologies ranging from adsorption separations, sensing, and catalysis to solar cells and lithium-ion batteries. The goal of this proposed research project is to develop advanced multifunctional materials and processing techniques that can be used for the removal, detection, or destruction of chemical warfare agents (CWAs). The proposed work will build on our previous research on metal-organic frameworks for removal of ammonia, carbon monoxide, and other toxic chemicals. A particular emphasis will be placed on creating engineered forms and composites of multifunctional nanopowders that are suitable for use in low-pressure drop CWA removal devices or for incorporation into chemical sensing arrays.

### 1.3 OBJECTIVES

The goal of this work was to develop tools and processing techniques for the fabrication of MOF composites. The flexibility afforded by these synthesis techniques will lead to potential advances in materials for CWA removal, sensing, and destruction.

## 2.0 DELIVERABLES

### 2.1 MAJOR DELIVERABLES FOR YEAR 1

a) 3-6 new composites to be tested for adsorption of ammonia
b) Formation and characterization of 2-4 pelletized MOFs with different formulations of MMO or zirconium hydroxide binder and refinement of methods.
c) Testing of pelletized MOFs (minimum of 2-4 samples) for DMNP affinity and refine methods.

These deliverables resulted in a publication in I&EC Research: Mounfield et al., Synergistic Effect of Mixed Oxide on the Adsorption of Ammonia with Metal-Organic Frameworks, *Industrial & Engineering Chemistry Research*, 2016, 55, 6492—6600.

From the abstract: “A hydrotalcite-derived MgAl oxide (MMO) was evaluated in combination with the metal−organic frameworks (MOFs) UiO-66 and UiO-66-$NH_2$ for the adsorption of ammonia. Analysis of the materials’ textural properties after ammonia breakthrough adsorption revealed no change in the PXRD patterns or FTIR spectra; however, a slight decrease in surface area was
observed, consistent with the hypothesized presence of strongly adsorbed species after adsorption. UiO-66:MMO and UiO-66-$NH_2$:MMO composites maintained ammonia adsorption capacity under dry conditions. An almost 2-fold increase in humid ammonia capacity was observed for the UiO-66:MMO composite, far beyond that expected through a linear combination of the two materials’ capacities. The synergistic effect observed in humid conditions was further investigated with water adsorption experiments, which suggested the effect is the result of the high water affinity of MMO.”

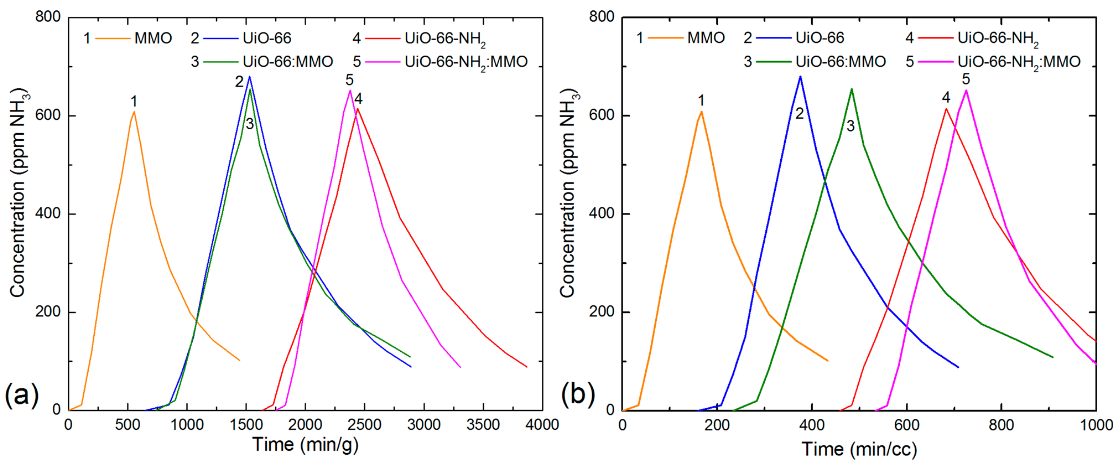
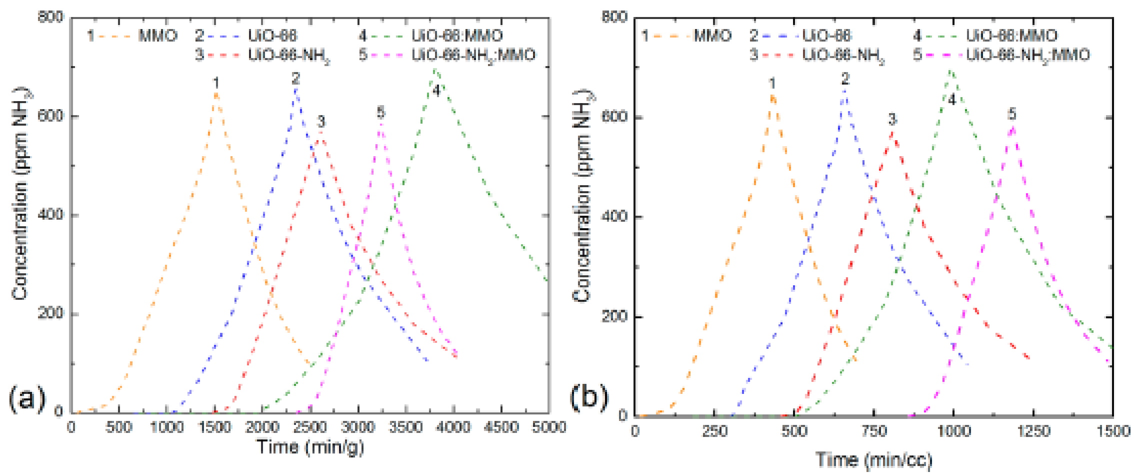



Figure 2 from the publication: Breakthrough and desorption curves for MMO, UiO-66, UiO-66-NH2, UiO-66:MMO, and UiO-66-NH2:MMO under dry conditions. Time is normalized either by (a) gram of total adsorbent mass in g or (b) total bed volume in $cm^3$.




Taken from Figure 3: Breakthrough and desorption curves for MMO, UiO-66, UiO-66-NH2, UiO-66:MMO, and UiO-66-NH2:MMO under wet conditions. Time is normalized either by (a) gram of total adsorbent mass in g or (b) total bed volume in cm3.

**Table 2. Calculated Dynamic Ammonia Capacity for All Materials and Composites[a]**

| material | dry $NH_3$ exposure capacity (mmol/g) | wet $NH_3$ exposure capacity (mmol/g) |
|---|---|---|
| UiO-66 | 1.84 | 2.63 |
| UiO-66-$NH_2$ | 3.25 | 3.18 |
| MMO | 0.68 | 1.50 |
| HT | 0.66 | 1.25 |
| UiO-66:MMO | 1.89 (2.26) | 5.06 (6.07) |
| UiO-66:HT | 1.51 (1.81) | 2.00 (2.40) |
| UiO-66-$NH_2$:MMO | 3.48 (4.18) | 4.06 (4.87) |

[a]Breakthrough capacity is calculated by extrapolation and integration to 1500/1483 ppm, respectively. Values shown in parentheses are normalized per gram of MOF.

Several major conclusions resulted from this work:

- Addition of MMO to UiO-66 in a 5:1 MOF:MMO ratio resulted in almost a 2-fold increase in wet ammonia adsorption performance above the pure MOF capacity, although the MMO alone possesses poor performance.
- The effect in humid conditions is hypothesized to be 2-fold, benefiting from a water withdrawing effect allowing adsorption sites to remain open for ammonia adsorption and the solubility of ammonia in the water adsorbed on the MMO.
- In dry conditions, the addition of MMO did not negatively affect adsorption performance, usually the case with the addition of a poorly adsorbing binding material.
- These composites showed promise as multiuse adsorbents, as the initial breakthrough capacity and synergistic effect was preserved through three consecutive exposures for the UiO-66:MMO composite in wet conditions.